

AMENDMENT  
(Under PCT Article 11)

TO: Examiner of the Patent Office: Kengo Koyanagi

1. Identification of the International Application  
PCT/JP2004/004533
2. Applicant  
Name: NIPPON STEEL CORPORATION  
Address: 6-3, Otemachi 2-Chome, Chiyoda-ku, Tokyo  
100-8071 Japan  
Country of nationality: JAPAN  
Country of residence: JAPAN
3. Agent  
Name: (9975) Patent Attorney, AOKI Atsushi

stamp

Address: A. AOKI, ISHIDA & ASSOCIATES  
Toranomom 37 Mori Bldg., 5-1  
Toranomom 3-Chome, Minato-ku  
TOKYO 105-8423 Japan

4. Item to be Amended: (1) Specification  
(2) Claims
5. Subject Matter of Amendment  
(1) Page 6, line 5 to page 7 line 15 in the  
specification is amended as attached.  
(2) Page 12, line 34 to page 13, line 1 "and manganese  
aluminum silicate, but in this case the oxide particles have  
to be added to the plating bath or the main ingredient  
elements of the oxide have to be added to the steel sheet -  
inviting a rise of the production costs" is amended to "and

EXPRESS MAIL NO. EV 320247633 45

manganese aluminum silicate".

(3) Page 16, lines 8 to 9 "plating layer, but some of the oxide particles may remain in the steel sheet." is amended to "plating layer, but some of the oxide particles may remain in the steel sheet, or may exist at the interface between the plating layer and the steel sheet.".

(4) Delete claim 8 and claims 1 and 3 - 7 are amended as attached.

(5) As a result of deletion of claim 8, page 24 is omitted.

6. Attachment

- |                         |       |
|-------------------------|-------|
| (1) New pages 6 and 7   | 1 set |
| (2) New pages 12 and 13 | 1 set |
| (3) New page 16         | 1 set |
| (4) New pages 22 to 23  | 1 set |

layer containing oxide particles of at least one type of oxide selected from an Al oxide, Si oxide, Mn oxide, Al and Si complex oxide, Al and Mn complex oxide, Si and Mn complex oxide, and Al, Si, and Mn complex oxide alone or in combination, and an average diameter of the particle size of said oxide is 0.01 - 1  $\mu\text{m}$ .

(2) An alloyed molten zinc plated steel sheet as set forth in (1), characterized in that said oxide particles are comprised of at least one of silicon oxide, manganese oxide, aluminum oxide, aluminum silicate, manganese silicate, manganese aluminum oxide, and manganese aluminum silicate.

(3) An alloyed molten zinc plated steel sheet as set forth in (1) or (2), characterized in that the structure of said steel sheet has a complex structure of a ferrite phase, bainite phase, and residual austenite phase.

(4) A process of production of an alloyed molten zinc plated steel sheet comprised of the ingredients described in (1) by a continuous molten zinc plating system, said process of production of an alloyed molten zinc plated steel sheet characterized by making a heating temperature T at a recrystallization annealing step in a reducing furnace of said system 650°C to 900°C, passing the steel sheet through an atmosphere where a ratio  $\text{PH}_2\text{O}/\text{PH}_2$  of the steam partial pressure  $\text{PH}_2\text{O}$  and hydrogen partial pressure  $\text{PH}_2$  of the atmosphere of said reducing furnace is  $1.4 \times 10^{-10}T^2 - 1.0 \times 10^{-7}T + 5.0 \times 10^{-4}$  to  $6.4 \times 10^{-7}T^2 + 1.7 \times 10^{-4}T - 0.1$ , forming internal oxide at a region from the surface of the steel sheet to a depth of 1.0  $\mu\text{m}$ , then successively performing molten zinc plating treatment and alloying treatment.

(5) A process of production of an alloyed molten

zinc plated steel sheet as set forth in (4), characterized in that said oxide particles are comprised of at least one of silicon oxide, manganese oxide, aluminum oxide, aluminum silicate, manganese silicate, manganese aluminum oxide, and manganese aluminum silicate.

(6) A process of production of an alloyed molten zinc plated steel sheet as set forth in (4), characterized in that an average diameter of the particle size of said oxide is 0.01 to 1  $\mu\text{m}$ .

(7) A process of production of an alloyed molten zinc plated steel sheet as set forth in any one of (4) to (6), characterized in that the structure of said steel sheet has a complex structure of a ferrite phase, bainite phase, and residual austenite phase.

#### BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a schematic view of an example of the cross-section of an alloyed molten zinc plated steel sheet of the present invention.

#### BEST MODE FOR CARRYING OUT THE INVENTION

The alloyed molten zinc plated steel sheet of the present invention is characterized by being provided with both a superior press formability and strength and by having an area occupied by the parts where the Fe-Zn alloy phase is not formed in the plating layer of less than 10% of the area of the steel sheet as a whole.

To impart this characterizing feature, first, to secure the ductility and strength of the steel sheet itself, the ingredients of the steel sheet are made, by wt%, C: 0.05 to 0.40%, Si: 0.2 to 3.0%, Mn: 0.1 to 2.5%, and the balance of Fe and unavoidable impurities, while the structure of the steel sheet is made a complex phase structure including the ferrite phase, bainite phase, and austenite phase. Note that the contents of the steel composition defined in the present invention are all wt%.

The reasons for addition of the additive elements to the steel sheet base material of the alloyed molten zinc

assaying the concentration of Fe in the plating layer by glow discharge optical emission spectrometry. At this time, the size of each analysis point is made a constant diameter of 5 mm. Cases where at least nine locations  
5 having concentrations of Fe in the plating layer of 7 to 15 wt% are judged as passing and other cases are judged as failing. Cases where there are two or more locations where the concentration of Fe in the plating layer is less than 7 wt% are judged as being insufficiently  
10 alloyed and as therefore failing, while cases where there are two or more locations where the concentration is over 15 wt% are judged as being excessively alloyed.

The Al oxide, Si oxide, Mn oxide, Al and Si complex oxide, Al and Mn complex oxide, Si and Mn complex oxide,  
15 and Al, Si, and Mn complex oxide contained in the plating layer are respectively silicon oxide, manganese oxide, aluminum oxide, aluminum silicate, manganese silicate, manganese aluminum oxide, and manganese aluminum silicate. Si, Mn, and Al are elements added as  
20 ingredients of the steel sheet. These become oxides at the surface layer of the steel sheet in the heat treatment step of the steel sheet. They can be easily included in the plating layer for forming silicon oxide, manganese oxide, aluminum oxide, aluminum silicate,  
25 manganese silicate, manganese aluminum oxide, and manganese aluminum silicate. The method for including the oxide particles in the plating layer will be explained later.

Note that the oxide particles to be contained in the  
30 plating layer to promote the alloying of Fe and Zn of the plating layer may also be oxides other than the above silicon oxide, manganese oxide, aluminum oxide, aluminum silicate, manganese silicate, manganese aluminum oxide, and manganese aluminum silicate.

The size of the oxide particles contained in the plating layer is preferably an average diameter of 0.01  $\mu\text{m}$  to 1  $\mu\text{m}$ . The reason is that if the average diameter of the oxide particles is less than 0.01  $\mu\text{m}$ , the effect of causing uniform alloying of Fe-Zn in the plating layer falls. If making the average diameter of the oxide particles more than 1  $\mu\text{m}$ , at the time of processing the alloyed molten zinc plated steel sheet, the oxide particles easily become starting points of fracture and the corrosion resistance of the processed parts is degraded, that is, detrimental effects easily occur when putting the molten zinc plated steel sheet into practical use.

Note that the "average diameter" of the oxide particles referred to in the present invention indicates the average equivalent circular diameter of the oxide particles detected by observation of the cross section of the plating layer. The shape of the oxide particles may be spherical, plate-like, or conical.

As the method of measuring the average diameter of the oxide particles, the method may be mentioned of polishing the cross section of the alloyed molten zinc plated steel sheet or using FIB (focused ion beam processing system) to process the sheet to expose the cross section and thereby prepare a sample, then analyzing it by observation by a scan electron microscope, plane analysis by X-ray microanalysis, or plane analysis by Auger electron spectroscopy. Further, it is possible to process the cross section of the steel sheet to a thin piece so as to include the plating layer, then observe this by a transmission type electron microscope. In the present invention, the image data obtained by these analysis methods is analyzed to calculate the equivalent circular diameter of the oxide particles. The average value should be 0.01  $\mu\text{m}$  to 1  $\mu\text{m}$ .

layer to form the characteristic of the alloyed molten zinc plated steel sheet of the present invention, that is, the plating layer structure containing oxide particles in a plating layer.

5 In the case of forming the above mentioned plating layer structure, all oxide particles formed at the surface of the steel sheet do not always move into the plating layer, but some of the oxide particles may remain in the steel sheet, or may exist at the interface between  
10 the plating layer and the steel sheet.

In the present invention, Fe and Zn alloying is promoted by the action of the oxide particles contained in the plating layer. If the heating temperature and holding time are in the above range in the alloying step,  
15 sufficiently uniform alloying is possible. Therefore, it is possible to finish the alloying treatment while the austenite phase in the steel sheets is not reduced. Consequently, steel sheets having the desired mixed structures of the ferrite phase, bainite phase, and  
20 austenite phase can be obtained.

#### Examples

Below, the present invention will be explained in detail by examples, but the present invention is not limited to these examples.

25 The test steel sheets shown in Table 1 were treated for recrystallization annealing, plating, and alloying by a continuous molten zinc plating system in accordance with the conditions shown in Table 2.

Table 1

Test mater- ial code	Composition (wt%)										Remarks
	C	Si	Mn	Al	P	S	Ti	Nb	Ni	Cu	
NA	0.1	1.2	1.3		0.004	0.003					Invention
A	0.1	0.2	1.6	0.1	0.005	0.006	0.02		0.6	0.2	Invention
B	0.1	0.2	1.5	0.7	0.005	0.007	0.02	0.01	0.01	0.2	Invention
C	0.1	1.5	1.5	0.03	0.005	0.006			0.002		Invention
D	0.05	1.4	2.3	0.3	0.005	0.007					Invention
E	0.1	1.5	0.5	0.2	0.004	0.006					Invention
F	0.1	0.1	1.4	0.4	0.006	0.003					Comp. ex.

CLAIMS

1. (Amended) An alloyed molten zinc plated steel sheet characterized by comprising a steel sheet including, by wt%,

5 C: 0.05 to 0.40%,  
Si: 0.2 to 3.0%, and  
Mn: 0.1 to 2.5% and  
further including at least one or two or more

types of:

10 P: 0.001 to 0.05%,  
S: 0.001 to 0.05%,  
Al: 0.01% to 2%,  
B: 0.0005% to less than 0.01%,  
Ti: 0.01% to less than 0.1%,  
15 V: 0.01% to less than 0.3%,  
Cr: 0.01% to less than 1%,  
Nb: 0.01% to less than 0.1%,  
Ni: 0.01% to less than 2.0%,  
Cu: 0.01% to less than 2.0%,  
20 Co: 0.01% to less than 2.0%,  
Mo: 0.01% to less than 2.0%,

with the balance comprised of Fe and  
unavoidable impurities, having on its surface a Zn alloy  
plating layer comprised of Fe in a concentration of 7 to  
25 15 wt%, Al in a concentration of 0.01 to 1 wt%, and the  
balance of Zn and unavoidable impurities, said plating  
layer containing oxide particles of at least one type of  
oxide selected from an Al oxide, Si oxide, Mn oxide, Al  
and Si complex oxide, Al and Mn complex oxide, Si and Mn  
30 complex oxide, and Al, Si, and Mn complex oxide alone or  
in combination, and an average diameter of the particle  
size of said oxide is 0.01 - 1  $\mu$ m.

2. An alloyed molten zinc plated steel sheet as  
set forth in claim 1, characterized in that said oxide  
35 particles are comprised of at least one of silicon oxide,  
manganese oxide, aluminum oxide, aluminum silicate,  
manganese silicate, manganese aluminum oxide, and



- 22/1 -

manganese aluminum silicate.

3. (Amended) An alloyed molten zinc plated steel sheet as set forth in claim 1 or 2, characterized in that the structure of said steel sheet has a complex structure of a ferrite phase, bainite phase, and residual austenite phase.

5 4. (Amended) A process of production of an alloyed molten zinc plated steel sheet comprised of the ingredients described in claim 1 by a continuous molten zinc plating system, said process of production of an  
10 alloyed molten zinc plated steel sheet characterized by making a heating temperature T at a recrystallization annealing step in a reducing furnace of said system 650°C to 900°C, passing the steel sheet through an atmosphere where a ratio  $\text{PH}_2\text{O}/\text{PH}_2$  of the steam partial pressure  $\text{PH}_2\text{O}$   
15 and hydrogen partial pressure  $\text{PH}_2$  of the atmosphere of said reducing furnace is  $1.4 \times 10^{-10}T^2 - 1.0 \times 10^{-7}T + 5.0 \times 10^{-4}$  to  $6.4 \times 10^{-7}T^2 + 1.7 \times 10^{-4}T - 0.1$ , forming internal oxide at a region from the surface of the steel sheet to a depth of 1.0  $\mu\text{m}$ , then successively performing molten zinc plating  
20 treatment and alloying treatment.

5. (Amended) A process of production of an alloyed molten zinc plated steel sheet as set forth in claim 4, characterized in that said oxide particles are comprised of at least one of silicon oxide, manganese  
25 oxide, aluminum oxide, aluminum silicate, manganese silicate, manganese aluminum oxide, and manganese aluminum silicate.

6. (Amended) A process of production of an alloyed molten zinc plated steel sheet as set forth in  
30 claim 4, characterized in that an average diameter of the particle size of said oxide is 0.01 to 1  $\mu\text{m}$ .

7. (Amended) A process of production of an alloyed molten

zinc plated steel sheet as set forth in any one of claims 4 to 6, characterized in that the structure of said steel sheet has a complex structure of a ferrite phase, bainite phase, and residual austenite phase.